

Experimental and simulation studies on mineral trapping of CO₂ with brine

Y. Soong ^{*}, A.L. Goodman, J.R. McCarthy-Jones, J.P. Baltrus

U.S. Department of Energy, National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236 0940, USA

Abstract

The reaction of carbon dioxide (CO₂) with brine samples collected from the Oriskany Formation in Indiana County, PA, was investigated in an autoclave reactor under various conditions. A geochemical code, PHREEQC, was used as to simulate the reaction in the autoclave reactor. The combined experimental and modeling data suggests that pH (pH > 9) plays a key role in the formation of carbonate minerals. The effects of temperature and CO₂ pressure have a lesser impact on the formation of carbonate minerals.

Keywords: Brine; Mineral trapping; Carbonates

1. Introduction

Carbon dioxide (CO₂) is the main contributor to global warming [1]. CO₂ is primarily emitted into the atmosphere from combustion of fossil fuels in power plants. Many techniques to capture and store CO₂ are currently being investigated. It is believed that permanent sequestration of CO₂ can reduce the greenhouse effects generated from fossil fuel combustion. CO₂ injection into saline aquifer formations is one of the most promising geologic CO₂ sequestration options. It offers two major advantages: first, the estimated carbon storage capacity of saline aquifer formations in the United States is large (500 Gt. of CO₂), making them a viable long term solution, and second,

^{*} Corresponding author. Tel.: +1-412-386-4925; fax: +1-412-386-4806/396-4810.
E-mail address: soong@netl.doe.gov (Y. Soong).

most existing large CO₂ point sources are located near saline aquifer formations, making CO₂ transportation costs minimal. Therefore, sequestration of CO₂ into saline aquifer formations is an important strategy to mitigate global warming [1,2].

Upon injection of CO₂ into saline aquifers, CO₂ may be stored by hydrodynamic, solubility and mineral trapping. In hydrodynamic and solubility trapping, CO₂ is captured in saline aquifers as a fluid (CO_{2(l)}) or aqueous component (H₂CO₃, HCO₃⁻, CO₃⁼ and CO_{2(aq)}). The most critical concern of hydrodynamic trapping is the potential for CO₂ leakage through imperfect confinement. The main issue that affects solubility trapping is the limited CO₂ solubility in brine. In mineral trapping, CO₂ is converted into carbonate minerals by a series of reactions with aqueous ions found in the saline aquifer. Various carbonates such as calcite (calcium carbonate), magnesite (magnesium carbonate), dolomite (calcium–magnesium carbonate) and siderite (iron carbonate), can be formed in the brine aquifer by mineral trapping. These carbonate minerals can be stored in saline aquifer formations for millions of years [1–4]. However, conversion of CO₂ to stable carbonate minerals is expected to be slow. The Alberta Research Council in Canada [4] conducted a computer simulation of the mineral trapping process (kinetic water–rock reaction model, PATHARC.94) under reservoir conditions. These authors calculated times for precipitation of the various carbonates on the order of hundreds of years. These results suggest that mineral trapping conversion of CO₂ to carbonate minerals may contribute significantly to CO₂ sequestration within saline aquifers but only in the very long term.

Some researchers have conducted mineral trapping studies in the laboratory. Sass et al. [5] studied CO₂ and brine reactions with mineral rocks for 7 days at a pressure of 5.44 MPa and 110 °C. They found increased levels of calcium, magnesium and carbonate in solution, which were due to the dissolution of dolomite. They interpreted the decreased aqueous calcium and sulfate concentrations as evidence for anhydrite precipitation. Lebro'n and Suarez [6] reported the precipitation rate of calcite increased as the partial pressure of CO₂ increased (0.035–10 kPa). Their interpretation suggested that by increasing the partial pressure of CO₂, the solution pH decreases and the ionic strength increases. These conditions strongly influence nucleation of new calcite crystals. However, no extensive laboratory studies directed at the sequestration of CO₂ in brine aquifers have been conducted. In this study, the physical and chemical properties of brine from the Oriskany Sandstone aquifer of the Appalachian Basin are examined to assess its potential to sequester CO₂ in the near term via the mineral trapping pathway upon reaction with CO₂. This study attempts to evaluate the ability of such brines alone to serve as a mineral trapping medium. It is prudent to investigate the variables that effect mineral carbonates formation in brines in the absence of interference introduced by the presence of formation rocks. Once these effects are clearly defined, then experiments that include rock will be undertaken. The computer program PHREEQC version 2 also modeled carbonation of Oriskany Formation brine. PHREEQC version 2 is a computer program that is designed to perform a wide variety of low temperature aqueous geochemical calculations. The PHREEQC computer program and manual can be obtained from the USGS web site [7].

In this study, we explored the mineral trapping pathway for the reaction of CO₂ with brine samples. The optimum reaction conditions that favor the formation of mineral carbonates were investigated with autoclave experiments and geochemical modeling with PHREEQC [7]. Specifically, the effects of pH, CO₂ pressure and temperature on the reaction between CO₂ and brine samples to form carbonate minerals were investigated.

2. Experimental apparatus and procedure

To examine the process of mineral trapping under controlled temperature and pressure conditions in an autoclave reactor, brine samples were collected from the Oriskany Sandstone aquifer in Indiana County, PA. Samples were collected directly from the well after purging at a formation depth of 2800 m. The brine was collected in polyethylene bottles with air tight caps to reduce exposure to the atmosphere. The brine was tested as received without further filtration. Although there are some inherent sampling problems with surface collection of brines from subsurface environments such as changes from in situ subsurface temperatures and pressures, the sampling generally followed the accepted procedures for brine collection presented by Lico and others [8]. It is believed that this should minimize the differences between in situ brine chemistry and those analyzed in the laboratory.

Brine carbonation experiments were conducted in a 1/2 l autoclave (Hastelloy C-276) manufactured by Progressive Equipment Corp. In a representative experiment, the reactor was charged with 180 ml of brine. The reactor was purged/evacuated with carbon dioxide three times. Finally, a predetermined amount of CO₂ was charged into the reactor to achieve the desired testing pressure. The brine–CO₂ mixture was agitated at 400 or 800 rpm during both heating to the desired temperature and testing to prevent any settling of precipitate. At the completion of each test, the slurry was cooled to room temperature. The remaining CO₂ was vented, and the slurry was removed from the reactor and filtered to separate the solids from the aqueous solution. A digital pH meter (Sentron-1001 pH) was used to determine the pH of the brine before and after reaction. The pH meter was calibrated with buffer solutions before each measurement. The brine was used either as received, or the pH was adjusted before reaction by adding KOH. The effects of pH (3.6–11), reaction time (1–6 h), CO₂ pressure (0.34–7.63 MPa) and temperature (50–170 °C) on brine carbonation were investigated.

The brines and brine products were prepared for analysis by filtration through a 0.45 µm membrane (Millipore-type HA) aided by reduced pressure provided by a water aspirator. The collected solids were rinsed with deionized water on the membrane and dried in a nitrogen purged oven at 110 °C. The filtered solutions were acidified (pH < 2.0) by adding trace metal grade nitric acid. Because of the high concentration of alkali and alkaline earth metals in solutions, 200-fold dilutions were prepared using distilled, deionized water. Metal concentrations were then determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Optima 3000 ICP spectrometer. The determinations were performed using an online internal standard to correct for variations during sample introduction. The reproducibility of the analytical results for cations by ICP is with a detection limit of approximately ±3% for the elements measured. A low flow gem cone nebulizer was employed so that solids loading could be accommodated, and a glass cyclonic spray chamber was employed to minimize contamination between analyses.

X-ray diffraction (XRD) measurements were conducted using a Rigaku DAD-IIA powder diffractometer with a Cu-Kα X-ray source at 40 kV and 25 mA. The powder sample was mounted on a glass sample holder. The XRD patterns were recorded over a 2θ range of 2–90° and compared with the JCPDS mineral powder diffraction file. A single crystalline phase must have a concentration of approximately 5 wt.% in order to be detected.

X-ray photoelectron spectroscopy (XPS) analyses were conducted, using a PHI 5600ci spectrometer. A monochromatic Al Kα (1486.6 eV) X-ray source was used at power of 400 W, with

the analysis chamber typically maintained at less than 1×10^{-8} Torr. The pass energy of the analyzer was 58.7 eV. Samples were analyzed after dusting them onto doublesided conductive sticky tape. The reproducibility of the XPS measurements is typically $\pm 10\%$ with a detection limit of 0.3% atomic.

FT-IR spectra were acquired using a Nicolet Nexus 670 FT-IR equipped with an attenuated total reflectance (ATR) accessory. The investigated range was from 4000 to 400 cm^{-1} . The signal was obtained by averaging 16 scans at a resolution of 4 cm^{-1} . The detection limit for carbonate using FTIR is approximately 0.1% (wt.).

The brine carbonation reactions were also modeled with the computer program PHREEQC version 2. It should be noted that the application of PHREEQC to model high saline solutions is limited because PHREEQC was designed to model natural waters at ambient temperatures.

3. Results

Preliminary autoclave experiments were conducted to investigate the effect of pH and reaction time for the reaction of CO_2 with brine samples. The pH experiments were conducted in two ways: the brine was used as received (pH = 3.9) before reaction with CO_2 (Rxn 1: 155°C , 6.19 MPa of CO_2 , 400 rpm and 1 h), and the pH of the brine was adjusted with KOH to pH 11.0 before reaction with CO_2 (Rxn 2: 155°C , 4.6 MPa of CO_2 , 400 rpm and 1 h). In general, the ionic concentrations of the aqueous brine solution changed very little between Rxn 1 and Rxn 2. However, the total amount of solid precipitate formed between Rxn 1 and Rxn 2 varied significantly—0.27 g/l of precipitate for (Rxn 1) versus 11.5 g/l of precipitate for (Rxn 2) (Fig. 1). The composition of the solid precipitate also varied with the reaction conditions. Under the conditions of Rxn 1, the composition of the solid precipitate was high in Na, Fe, Ba and Ca. However, when the pH was adjusted to pH = 11 prior to reaction (Rxn 2), the concentrations of Na, Ba and Fe in the pre-

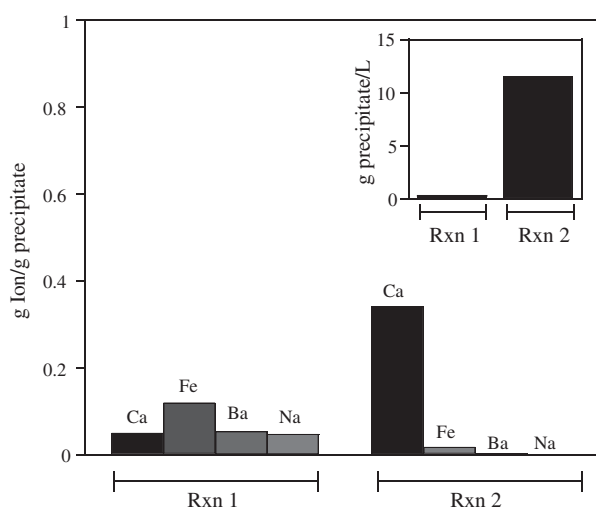


Fig. 1. Amounts of major cations present in precipitates from reactions (1) and (2).

precipitated solid were reduced by a factor of 100, while the concentration of Ca in the precipitated solid increased by a factor of 10. Thus, a higher initial pH results in more Ca in the precipitate.

The mineral composition of the precipitate from Rxn 1 and Rxn 2 was identified with XRD analysis. For the conditions in Rxn 1, the main mineral components identified were BaSO_4 , BaS_2O_7 and Fe_2O_3 . No carbonate minerals were detected in the analysis for Rxn 1. This is expected because the pH of the brine solution is too low to stabilize carbonate minerals. Carbonate minerals are soluble in acidic solutions and, thus, are not expected to precipitate. For the conditions in Rxn 2, solid components CaCO_3 (major) and Fe_2O_3 (minor) were identified with XRD. There was no observation for other carbonate mineral formation such as FeCO_3 , BaCO_3 and MgCO_3 . In general, the net increase in solid precipitate between Rxn 1 and Rxn 2 is probably due to the precipitation of CaCO_3 .

A series of autoclave experiments to study the effect of reaction time for formation of carbonate minerals were conducted (Fig. 2). The autoclave reaction conditions were set at 155 °C, 6.87 MPa of CO_2 , pH 11.0 and 800 rpm. The reaction time was ranging from 1 to 6 h. In the aqueous phase, the most noticeable change was found in the Ca concentration after 4 h of reaction. The Ca concentration decreased by 20%. The average total amount of solid precipitate was around 8.88 g/l after 3 h of reaction. The largest changes in the solid precipitate composition versus reaction time were for the Ca. The amount of Ca precipitate increased with reaction time. After 6 h of reaction time, the amount of Ca precipitate in the form of CaCO_3 leveled off. Furthermore, no additional significant changes in the results of our experiments beyond a reaction time of 6 h were observed. Thus, we concluded that the optimum reaction time for formation of CaCO_3 in the autoclave reactor was between 4 and 6 h.

Next the reaction of CO_2 with brine samples was investigated as a function of pH, temperature and CO_2 pressure with both autoclave reactor experiments and geochemical model. In the simulation input, the mineral dolomite was not allowed to precipitate even though the saturation index for this mineral was positive. According to Lasaga's work [9], the kinetics for dolomite precipi-

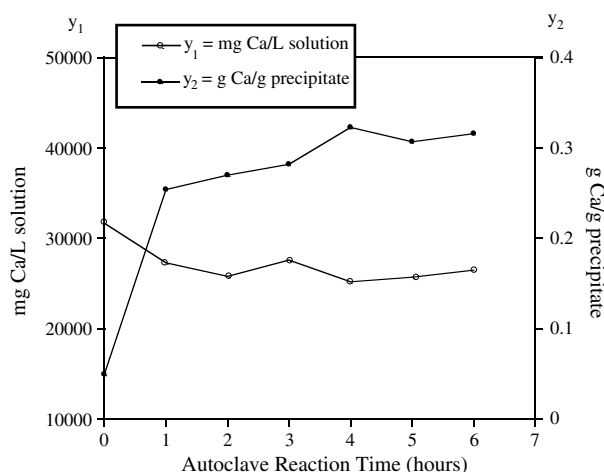


Fig. 2. Concentrations of Ca present in solution and precipitate as a function of reaction time (155 °C, 6.87 MPa of CO_2 , 800 rpm and pH 11).

tation is relatively slow, and it is likely that this mineral may not precipitate out of solution. In addition, XRD analysis of the solid precipitate from the autoclave reactions did not detect dolomite.

A series of autoclave experiments and simulations were conducted to study the reaction of CO_2 with brine samples as a function of pH at constant temperature (155°C) and CO_2 pressure (6.87 MPa) (Fig. 3). In the autoclave experiments, the initial pH was adjusted from 3.6 to 11.0 by adding KOH. After reaction, the pH of the solution was measured and found to be lower than the starting pH (Fig. 3a—solid circles). A similar trend between the pH before reaction and the pH after reaction with CO_2 is observed in the simulation results (Fig. 3a—dashed line). The pH of the brine decreases following reaction with CO_2 because CO_2 dissolves in solution to form carbonic acid, H_2CO_3 , thus decreasing the pH. In addition, CO_2 was not present after reaction due to the reactor being depressurized. Ca and other metals are removed from solution by precipitation, the remaining solution becoming more acidic.

As the initial pH of the raw aqueous brine was increased from 3.6 to 11 in the autoclave experiments, the concentration of the aqueous ions Ca, Mg and Na in the reacted brine decreased by 25%, 17% and 17%, respectively. The total grams of precipitate increased from 0.08 to 7.5 g/l (Fig.

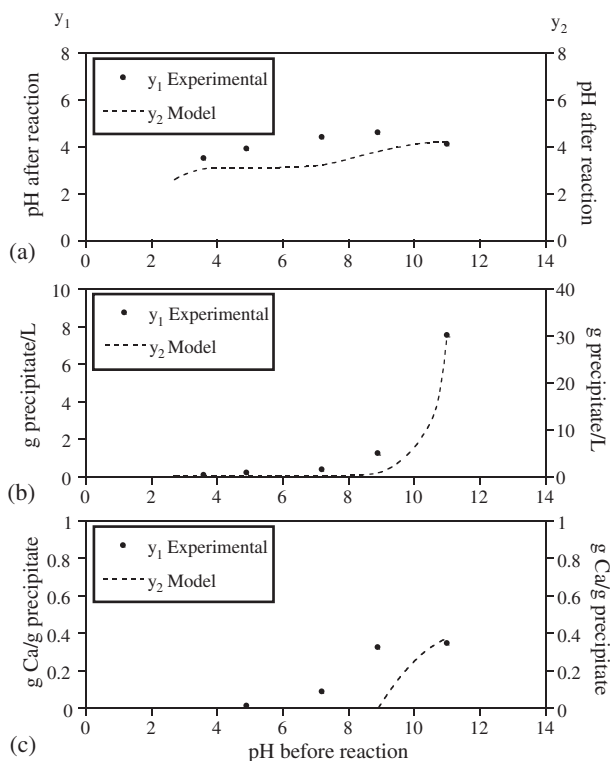


Fig. 3. Comparison of experimental and predicted results for brine carbonation as a function of pH under reaction conditions at 6.87 MPa CO_2 and 155°C . (a) pH after reaction versus pH before reaction. (b) Total grams of precipitate per liter of solution versus pH before reaction. (c) Grams of precipitated Ca^{2+} per total grams of precipitate versus pH before reaction.

3b—solid circles). The simulation results indicate a similar trend in that, as pH increases, the total grams of solid precipitate increases from 0.1 g at pH 2.7 to 30.5 g at pH 11 (Fig. 3b—dashed line). However, the total grams of precipitate predicted by the model deviates very significantly from the experimental observations in that the model predicts almost four times as much solid precipitate as was observed experimentally. This may be due to the fact that the simulation is predicting the total grams of precipitate under equilibrium conditions at 155 °C, while the total grams of solid precipitate from the autoclave experiments is measured after 6 h of reaction followed by degassing CO₂ and cooling to room temperature. Although the experimental and model results differ on the amount of solid precipitate formed as pH is increased, both results follow the same general trend in that the total mass of solid precipitate increases as the pH increases (Fig. 3b). Only 0.09 g of Ca per gram of precipitate was observed at the initial brine pH of 7.2. Significantly more Ca precipitate was observed after the initial brine pH was increased to 9 and higher. The concentration of solid Ca precipitate also increased significantly as the initial brine pH was elevated (Fig. 3c). Thus, as the pH is increased from 9 to 11, the grams of CaCO₃ per total grams of precipitate (g Ca/g ppt) increases (Fig. 3c). It was calculated that 17% of the aqueous Ca ion was converted to solid Ca upon reaction with CO₂ at pH 11.0.

A thorough analysis of the precipitates, focusing on the extent of carbonate formation, at pH 9 and pH 11 was accomplished using XRD, FT-IR and XPS. The XRD results indicated that CaCO₃ was the major (95% by weight) crystalline component of the precipitate, with the remainder being Fe₂O₃. Both FT-IR and XPS results were consistent with the XRD results and provided additional information. The FT-IR spectra in Fig. 4 show bands at 1394, 874 and 713 cm⁻¹. Each of these bands is characteristic of a carbonate species present in the precipitate. Note that all of these bands are sharper and more intense for the precipitate formed at the higher pH, indicative of greater carbonate formation. Fig. 5 shows the XPS C 1s spectra of the corresponding precipitates. The peak at 284.6 eV is typically assigned to adventitious carbon found in all samples exposed to the atmosphere. The peak at 289.1 eV is due to the presence of carbonate. The carbonate peak has greater overall absolute intensity, as well as relative intensity, compared to the 284.6 eV peak for the pH 11 precipitate. This is again consistent with greater carbonate formation at pH 11.

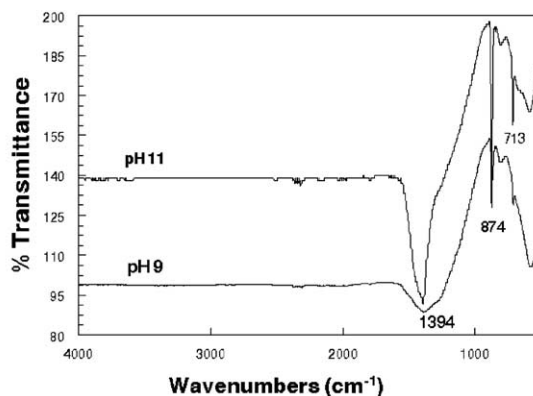


Fig. 4. FT-IR spectra of brine precipitates formed at pH 9 and pH 11.

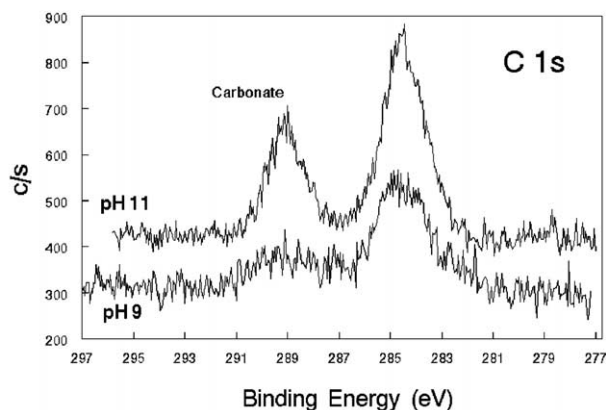


Fig. 5. XPS C 1s spectra of brine precipitates formed at pH 9 and pH 11.

Next, a series of autoclave experiments and simulations were conducted to study the reaction of CO_2 with brine samples as a function of pressure at constant pH (pH = 11.0) and temperature (155 °C) (Fig. 6). The CO_2 pressure was varied from 0.34 to 7.64 MPa. The pH after reaction, concentration of the aqueous components, total grams of precipitate and grams of Ca per total grams of precipitate versus pressure did not change significantly as pressure was increased (Fig. 6a–c).

The FT-IR and XPS C 1s spectra of the precipitates formed during reaction at 0.89 and 7.55 MPa are shown in Figs. 7 and 8, respectively. In contrast to the differences in carbonate formation evidenced by the changes in spectral peak intensities upon increasing the pH from 9 to 11, any differences resulting from reaction under higher pressure are much less clear. Even in the absence of an internal standard, it was obvious that more carbonate was formed at the higher pH. Although there may be the appearance of slightly greater carbonate signal at higher pressure, the changes observed can be due to small changes in sampling volume or, in the case of XPS, simply more adventitious carbon at the lower pressure. In the absence of an internal standard, any perceived changes upon increasing the reaction pressure cannot be considered significant.

Based on all of these results, pressure does not seem to play a large role in the formation of carbonate minerals as long as a minimum CO_2 pressure is maintained in the reactor. Therefore, high CO_2 pressures are not required for the precipitation of carbonate minerals.

Finally, a series of autoclave experiments and simulations were conducted to study the reaction of CO_2 with brine samples as a function of temperature at constant pH (pH = 11.0) and CO_2 (0.34 MPa) pressure (Fig. 9). The temperature was varied from 50 to 170 °C. The pH after reaction, concentration of the aqueous components, total grams of precipitate and grams of Ca per total grams of precipitate versus temperature changed very little for the autoclave experiments (Fig. 9a–c).

The precipitates collected after reaction at 50 and 170 °C were analyzed by XRD. The results are presented in Figs. 10 and 11. For both precipitates, the major crystalline phase is clearly calcite. There was a trace amount of hematite formed at 170 °C (Fig. 11).

The simulation results predict a general increase in total grams of precipitate and grams of Ca per total grams of precipitate versus temperature. As mentioned earlier, this may be due to the

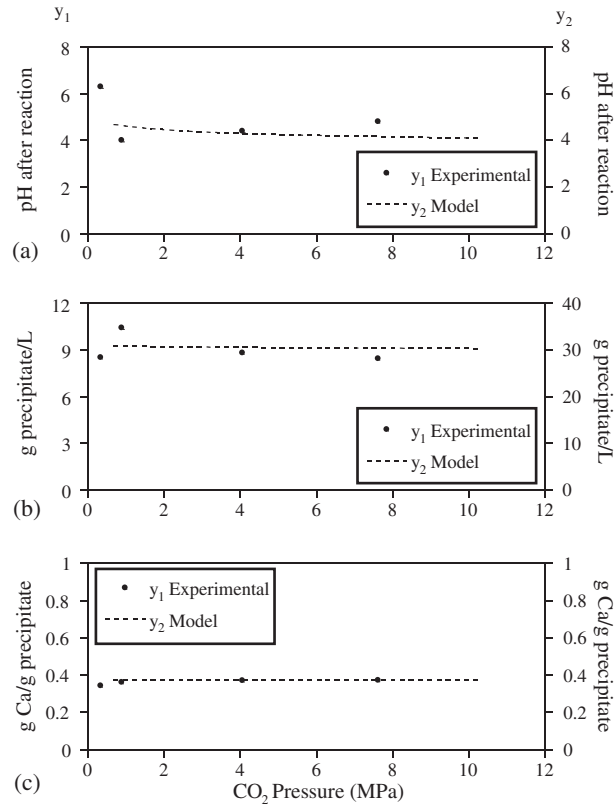


Fig. 6. Comparison of experimental and predicted results for brine carbonation as a function of CO₂ pressure at pH 11 and 155 °C. (a) pH after reaction versus CO₂ pressure. (b) Total grams of precipitate per liter of solution versus CO₂ pressure. (c) Grams of precipitated Ca²⁺ per total grams of precipitate versus CO₂ pressure.

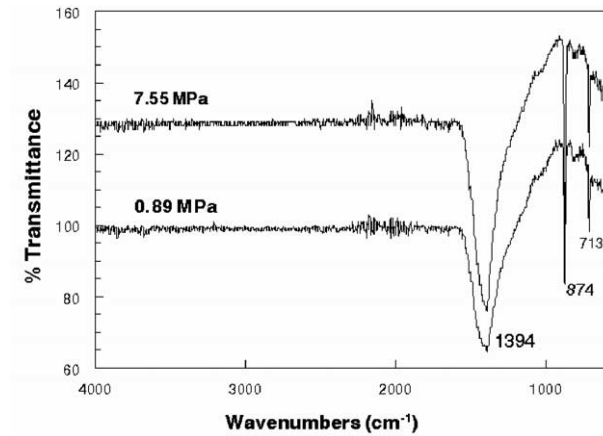


Fig. 7. FT-IR spectra of brine precipitates formed at CO₂ pressures of 0.89 and 7.55 MPa.

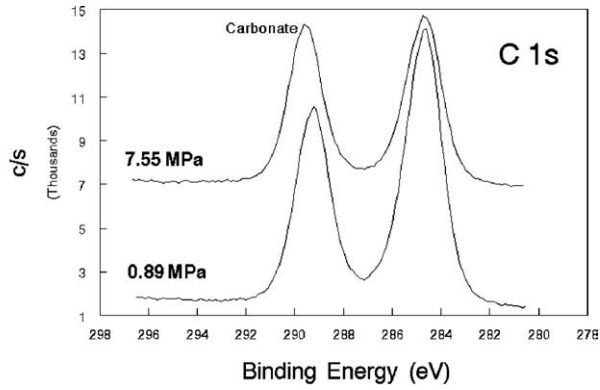


Fig. 8. XPS C 1s spectra of brine precipitates formed at CO₂ pressures of 0.89 and 7.55 MPa.

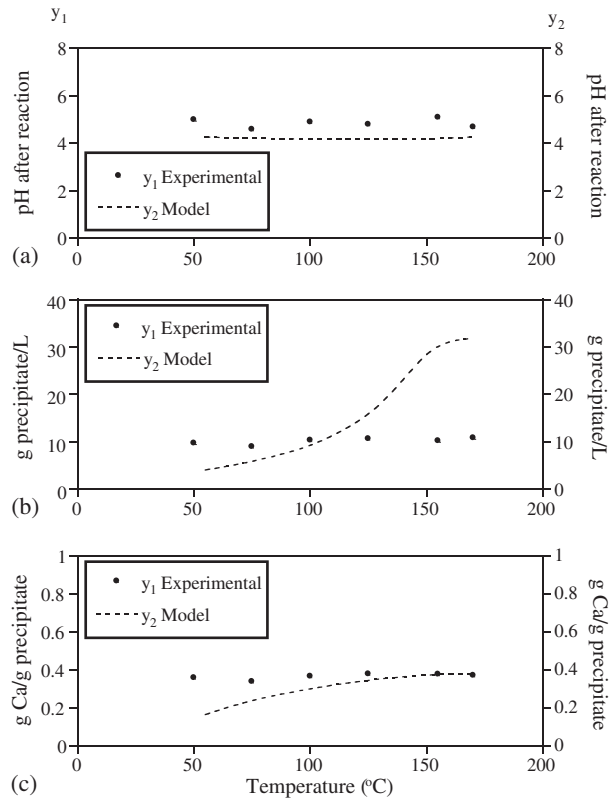


Fig. 9. Comparison of experimental and predicted results for brine carbonation as a function of temperature at 0.343 MPa CO₂ (autoclave experiments), 6.52 MPa CO₂ (PHREEQC model) and pH 11. (a) pH after reaction versus temperature. (b) Total grams of precipitate per liter of solution versus temperature. (c) Grams of precipitated Ca²⁺ per total grams of precipitate versus temperature.

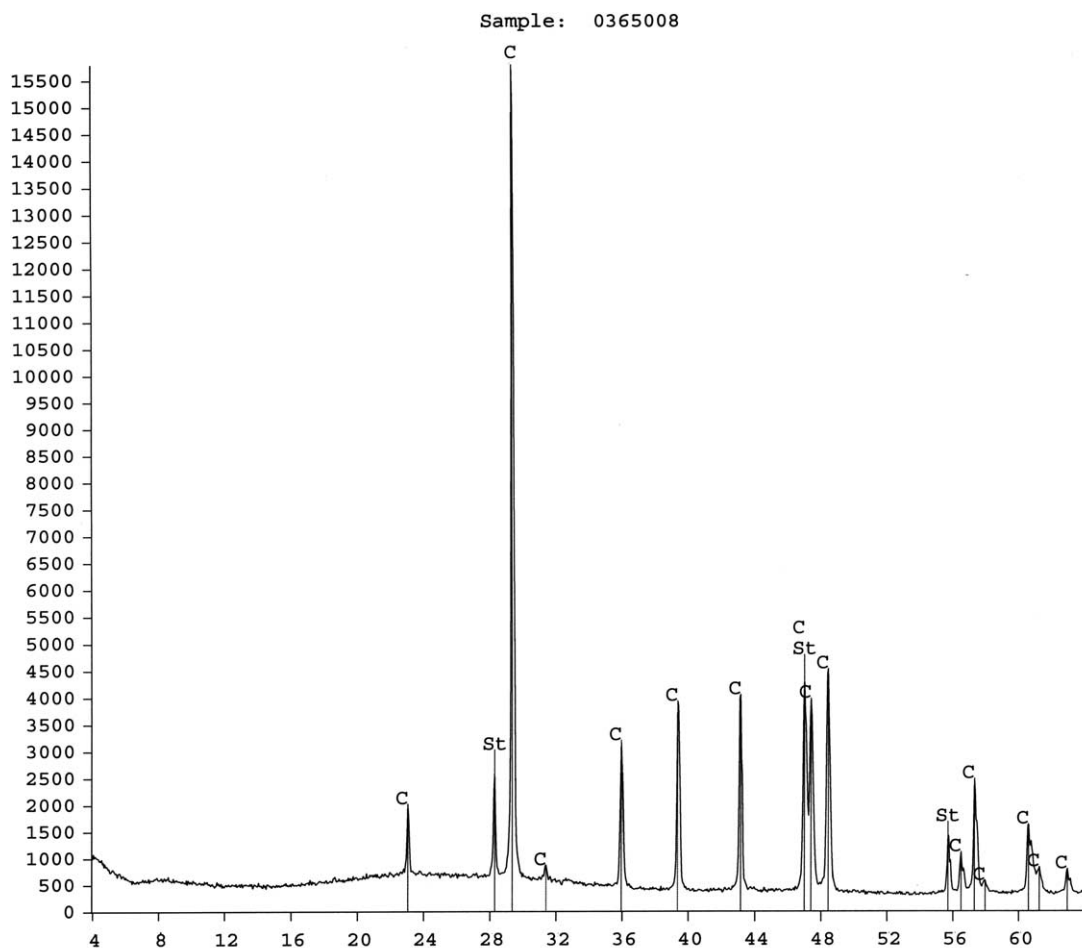


Fig. 10. XRD pattern of the brine precipitate formed at 50 °C (C—calcite, He—hermatite, St—strontianite).

fact that the simulation is predicting results under equilibrium conditions, while the data from the autoclave experiments is obtained after 6 h of reaction followed by degassing CO_2 and cooling from the reaction temperature to ambient conditions. The experimental results obtained under the conditions studied might be close to equilibrium, at best. From these results, the experimental data suggest that temperatures above 50 °C do not play a large role in the formation of carbonate minerals.

4. Discussions

Mineral trapping may occur via the simplified reactions (1)–(5) shown below. CO_2 gas dissolves into solution (1). Carbonic acid is formed (2), which then dissociates into bicarbonate (3) and carbonate ions (4). Thus, the pH of an aqueous solution decreases with the addition of CO_2 [10].

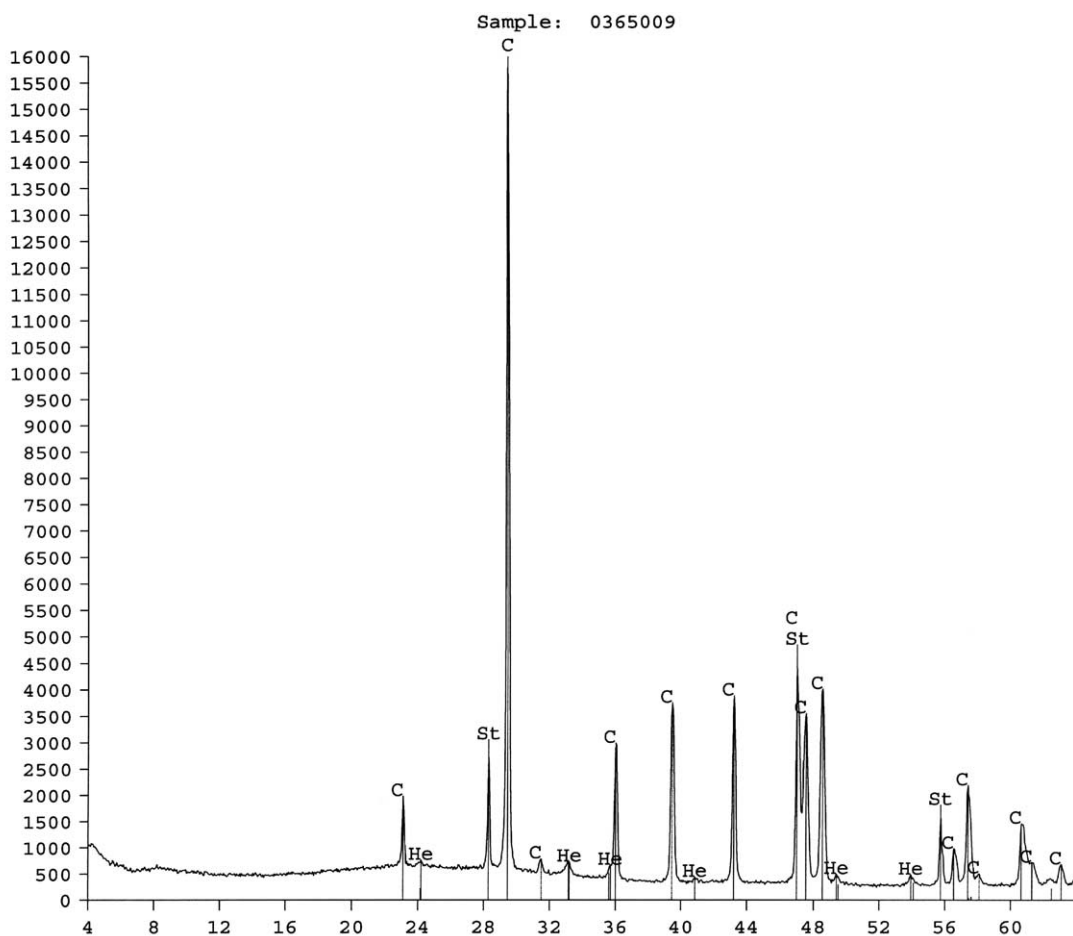
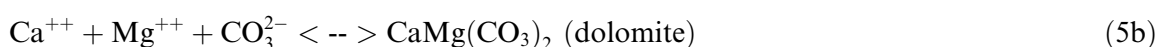


Fig. 11. XRD pattern of the brine precipitate formed at 170 °C (C—calcite, He—hermatite, St—strontianite).

Then, ions such as Ca, Mg and Fe react with the carbonate ions to form minerals, such as calcite, dolomite, siderite and magnesite (5a)–(5d), respectively.





The pH of the brine affects the reaction rate and species precipitated. In a closed system dissolved carbon dioxide, CO_2 (aq) and H_2CO_3 (carbonic acid) predominate at low pH HCO_3^- (bicarbonate) dominates at mid pH and CO_3^{2-} (carbonate) rules at high pH. Therefore, the solubility of carbonate increases as the pH decreases. Thus, aqueous phase equilibrium with CO_2 (g) promotes carbonate precipitation under basic conditions, while acidic conditions favor carbonate dissolution. In order to enhance the precipitation of mineral carbonates, the pH must be basic.

Mineral trapping is also controlled by CO_2 pressure and temperature but by a lesser extent when compared to pH. Temperature and pressure also play an important role in determining the solubility of CO_2 in solution [11]. The experimental results suggest that temperature does not play a major role in brine carbonation above 50 °C (Fig. 9). The CO_2 pressure affects the CO_2 brine reaction, but the reaction is more dependent upon pH. Dreybodt et al. [12] conducted a study of the precipitation kinetics of calcite in the system consisted of $\text{CaCO}_3\text{--H}_2\text{O--CO}_2$. They concluded that the rate limiting step is Eq. (3). Dunsmore [13] also indicated that the rate limiting step is the formation of HCO_3^- for calcium carbonate precipitation. If the same rate limiting step is applied to the CO_2 brine system, then the pH of the system would be the dominant factor affecting the reaction. Basic environments under high pH condition, pH = 11, provide an abundant supply of OH^- (aq) that reacts with H^+ and helps to shift the equilibrium in reactions (3) and (4) to the right. This, in turn, leads to the formation of HCO_3^- and CO_3^{2-} and finally the formation of CaCO_3 . The formation of calcite would ease once the OH^- (aq) was consumed. The pH also determines the amount of CO_2 that can be dissolved in brine. Therefore, pH has more impact on the carbonation reaction than the temperature and pressure. The overall simplified equilibrium equation for calcite formation can be described by Eqs. (6) and (7):



$$K = \frac{[\text{H}^+]^2}{[\text{Ca}^{2+}]P_{\text{CO}_2}} \quad (7)$$

According to Eq. (7), the calcite formation is dependent upon the hydrogen ion concentration, CO_2 pressure and Ca ion concentration. As shown in Fig. 6, when the CO_2 pressure increases, the amount of calcite precipitate remains the same. As the CO_2 pressure is increased, the pH decreases because carbonic acid is formed. As the CO_2 pressure continues to increase, the pH drops from 11 to around 4.5. At low pH values, calcite no longer precipitates from the solution. As discussed earlier, calcite precipitation is favored at high pH, while calcite dissolution is favored at low pH. Thus, the amount of Ca precipitate is limited by the pH not the CO_2 pressure as long as a minimum pressure is maintained. In order to increase the amount of CaCO_3 precipitation with increasing CO_2 pressure, the pH will need to be buffered at values higher than 9.0.

The only metal carbonate observed in the precipitates from this study was CaCO_3 . Several factors might contribute to this. First, the detection limits of the XRD utilized may not be sufficient to detect trace amounts of MgCO_3 and FeCO_3 . Second, the initial concentrations of Fe and Mg in the brine were too low to form stable carbonates based on the solubility product constants,

K_{sp} (MgCO₃ > CaCO₃ > FeCO₃) [14]. Since the ionic concentration of Ca is two orders of magnitude larger than that of Fe in the brine, given the same concentrations of CO₃⁼, CaCO₃ would precipitate instead of FeCO₃. Furthermore, MgCO₃ would not precipitate due to its relatively larger K_{sp} and low ionic strength in the brine.

The application of PHREEQC to model carbon sequestration is limited because PHREEQC was designed to model natural waters at ambient temperatures. Two of the most important concerns for modeling a CO₂/brine system with PHREEQC are the high ionic strength of the brine and the CO₂ pressure. PHREEQC uses ion-association and Debye–Huckel expressions to account for the non-ideality of aqueous solutions. This type of aqueous model is adequate at low ionic strength but may break down at the higher ionic strengths found in brine, (ionic strength > 0.26). All gas components in PHREEQC are assumed to behave according to the ideal gas law. The fugacity (activity) of a gas component is assumed to be equal to its partial pressure. For CO₂ pressures (3 MPa and greater) and temperatures (155 °C) used in this study, CO₂ does not behave as an ideal gas. At 25 °C and 5 MPa, for example, CO₂ deviates from the ideal gas law by a factor of 0.72. Because no off the shelf computer model is readily available and adequate to simulate the current experimental conditions (high saline contents, high pressures and high temperatures), the PHREEQC code was used only as a rough guide in predicting the experimental research. More advanced codes, such as PATHARC 94 [4,15] and SOLMINIQ [16] will be applied for future simulation work. In summary, the current simulation is not able to predict the exact experimental observations. However, the model is capable of demonstrating the general trends, such as the effects of pH and the CO₂ pressure on the mineral trapping process.

5. Conclusions

The reactions between CO₂ and brine samples collected from the Oriskany Formation in Indiana County, PA, were investigated experimentally using a 1/2 l autoclave under various conditions and theoretically using the geochemical code PHREEQC. The results of the experimental study show that the amount of calcite precipitate depends primarily on the pH of the brine. The CO₂ pressure and temperature have a lesser impact on the formation of carbonates. In addition, the simulation model used in this study is only able to predict the trends on the effects of pH and CO₂ pressure in the reactor.

References

- [1] DOE report, DOE/SC/FE-1, Carbon Sequestration Research and Development, December 1999.
- [2] Smith IM. CO₂ reduction—prospects for coal. IEA Coal Research; 1999.
- [3] Bergman PD, Winter EM. Energy Convers Manage 1995;36:523–6.
- [4] Hitchon B, Gunter WD, Gentzis T, Bailey RT. Energy Convers Manage 1999;40:825–43.
- [5] Sass BN, Gupta J, Ickes J, Egelhard M, Bergman P, Byaer C. Interaction of rock minerals with CO₂ and brine: a hydrothermal investigation. In: Conference Proceedings CD, 1st National Conference on Carbon Sequestration, Washington, DC, May 15–17, 2001.
- [6] Lebro'n I, Suarez DL. Geochim Cosmochim Acta 1998;62:405–16.
- [7] PHREEQC computer program USGS web site http://wwwbrr/cr.usgs.gov/projects/GWC_coupled.

- [8] Lico MS, Kharaka YK, Carothers WW, Wright VA. Methods for collection and analysis of geopressured geothermal and oil field waters. US Geological Survey Water-Supply Paper 2194, 1982. p. 21.
- [9] Lasaga AC. Kinetic theory in the earth science. Princeton University Press; 1998. p. 811.
- [10] Krauskopf KB. Introduction to geochemistry. 2nd ed. New York: McGraw-Hill; 1979. p. 43–4.
- [11] Enick BM, Klara SM. Chem Eng Commun 1990;90:23–31.
- [12] Dreybodd W, Eisenlohr L, Madry B, Ringer S. Geochim Cosmochim Acta 1997;61:3897–904.
- [13] Dunsmore HE. Energy Convers Manage 1992;33:565–72.
- [14] Lide DR. CRC handbook of chemistry and physics. 82nd ed., 2002.
- [15] Gunter WD, Wiwchar B, Perkins EH. Aquifer disposal of CO₂-rich greenhouse gases: extension of the time scale of experiment for CO₂-sequestrating reactions by geochemical modelling. Mineral Petrol 1997;59:121–40.
- [16] Kharaka YK, Gunter WD, Aggarwal PK, Perkins EH, DeBraal JD. SOLMINEQ.88 a computer program for geochemical modelling of water–rock interaction. US Geological Survey, Water Resource Investigation Report; 88-4227, 1988.